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December 30, 2003

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APPLICATION NUMBER: *60/419,390*
FILING DATE: *October 17, 2002*
RELATED PCT APPLICATION NUMBER: *PCT/US03/33006*

By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

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EXHIBIT
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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. ev 102704478 us

INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
Daniel	Alvarez, Jr.	San Diego, CA
Jeffrey J.	Spiegelman	San Diego, CA

☐ Additional inventors are being named on the _______ separately numbered sheets attached hereto

TITLE OF THE INVENTION (500 characters max)

CO2 PURIFICATION FOR THE SEMICONDUCTOR INDUSTRY

CORRESPONDENCE ADDRESS

Direct all correspondence to:

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ENCLOSED APPLICATION PARTS *(check all that apply)*

☑ Specification *Number of Pages* 10 — ☐ CD(s), Number

☑ Drawing(s) *Number of Sheets* 1 — ☑ Other (specify) return postcard

☐ Application Data Sheet. See 37 CFR 1.76

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

☑ Applicant claims small entity status. See 37 CFR 1.27.

☑ A check or money order is enclosed to cover the filing fees

☑ The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: 02-4070

☐ Payment by credit card. Form PTO-2038 is attached.

FILING FEE AMOUNT ($): $80.00

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☐ No.

☐ Yes, the name of the U.S. Government agency and the Government contract number are: ______________

Respectfully submitted,

SIGNATURE [signature]

Date 10/17/2002

TYPED or PRINTED NAME COLLEEN J. McKIERNAN

REGISTRATION NO. *(if appropriate)* 48,570

TELEPHONE 619-238-0999

Docket Number: 7184-PA18PR

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

PTO/SB/17 (11-01)
Approved for use through 10/31/2002. OMB 0651-0032
U S Patent and Trademark Office, U S. DEPARTMENT OF COMMERCE

FEE TRANSMITTAL for FY 2002

Patent fees are subject to annual revision

[X] Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT ($) 80

Complete if Known	
Application Number	unknown
Filing Date	unknown
First Named Inventor	Daniel Alvarez, Jr.
Examiner Name	unknown
Group Art Unit	unknown
Attorney Docket No.	7184-PA18PP

METHOD OF PAYMENT *(check all that apply)*

[X] Check [ ] Credit card [ ] Money Order [ ] Other [ ] None

[X] Deposit Account:

Deposit Account Number	02-4070
Deposit Account Name	Brown Martin Haller & McClain LL

The Commissioner is authorized to: *(check all that apply)*

[X] Charge fee(s) indicated below [X] Credit any overpayments

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FEE CALCULATION

1. BASIC FILING FEE

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
101	740	201	370	Utility filing fee	
106	330	206	165	Design filing fee	
107	510	207	255	Plant filing fee	
108	740	208	370	Reissue filing fee	
114	160	214	80	Provisional filing fee	80

SUBTOTAL (1) ($) 80

2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

			Extra Claims		Fee from below		Fee Paid
Total Claims		-20** =		X		=	0
Independent Claims		- 3** =		X		=	0
Multiple Dependent						=	0

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description
103	18	203	9	Claims in excess of 20
102	84	202	42	Independent claims in excess of 3
104	280	204	140	Multiple dependent claim, if not paid
109	84	209	42	** Reissue independent claims over original patent
110	18	210	9	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) ($) 0

**or number previously paid, if greater; For Reissues, see above

FEE CALCULATION (continued)

3. ADDITIONAL FEES

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
105	130	205	65	Surcharge - late filing fee or oath	
127	50	227	25	Surcharge - late provisional filing fee or cover sheet	
139	130	139	130	Non-English specification	
147	2,520	147	2,520	For filing a request for *ex parte* reexamination	
112	920*	112	920*	Requesting publication of SIR prior to Examiner action	
113	1,840*	113	1,840*	Requesting publication of SIR after Examiner action	
115	110	215	55	Extension for reply within first month	
116	400	216	200	Extension for reply within second month	
117	920	217	460	Extension for reply within third month	
118	1,440	218	720	Extension for reply within fourth month	
128	1,960	228	980	Extension for reply within fifth month	
119	320	219	160	Notice of Appeal	
120	320	220	160	Filing a brief in support of an appeal	
121	280	221	140	Request for oral hearing	
138	1,510	138	1,510	Petition to institute a public use proceeding	
140	110	240	55	Petition to revive - unavoidable	
141	1,280	241	640	Petition to revive - unintentional	
142	1,280	242	640	Utility issue fee (or reissue)	
143	460	243	230	Design issue fee	
144	620	244	310	Plant issue fee	
122	130	122	130	Petitions to the Commissioner	
123	50	123	50	Processing fee under 37 CFR 1 17(q)	
126	180	126	180	Submission of Information Disclosure Stmt	
581	40	581	40	Recording each patent assignment per property (times number of properties)	
146	740	246	370	Filing a submission after final rejection (37 CFR § 1 129(a))	
149	740	249	370	For each additional invention to be examined (37 CFR § 1 129(b))	
179	740	279	370	Request for Continued Examination (RCE)	
169	900	169	900	Request for expedited examination of a design application	

Other fee (specify) ____________________

*Reduced by Basic Filing Fee Paid

SUBTOTAL (3) ($) 0

SUBMITTED BY				Complete *(if applicable)*	
Name *(Print/Type)*	COLLEEN J. McKIERNAN	Registration No. *(Attorney/Agent)*	48,570	Telephone	619-238-0999
Signature	Collee			Date	10/17/2002

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CO_2 PURIFICATION FOR THE SEMICONDUCTOR INDUSTRY

BACKGROUND OF THE INVENTION

[0001] Carbon dioxide (CO_2) is used in a wide variety of industrial processes and products from the carbonation of beverages to the generation of semiconductors. In the semiconductor industry, CO_2 is used in wafer cleaning, for lens gases, laser gases, particle removal and plasma generation. Various phases of CO_2, liquid, gas and supercritical, are used dependent upon the application. Gases can be readily acquired that are $\geq$99.999% pure (contaminants $\leq$10 parts per million, ppm; Ultra High Purity). There is a need to further purify gases to $\leq$5 parts per billion (ppb) contaminants to meet the current Semiconductor Industry Association guidelines. Future requirements will be for contaminants of $\leq$1 ppb, preferably $\leq$ 0.1 ppb.

[0002] Precise decontamination protocols depend on the source of the CO_2 gas. However, regardless of the source, some contaminants are more difficult to remove than others including light hydrocarbons ($\leq C_4$), oxygen (O_2) and carbonyl sulfide (COS).

SUMMARY OF THE INVENTION

[0003] The invention is a method for the purification of CO_2 to achieve sufficient purity for use of the CO_2 in the semiconductor industry. The invention comprises the use of a combination of materials to achieve low contaminant levels. Decontamination can take place in any of a number of purification apparatuses including both bed and canister apparatuses. The contaminants of primary concern are O_2, sulfurous contaminants, especially COS, phosphorous containing contaminants, silicon containing contaminants and light hydrocarbons (LHC). Contaminants of secondary concern are nitrogenous contaminants, especially NH_3 and NO_x, and other organic compounds. In the method fo the invention, total contaminant levels are reduced to $\leq$ 5 ppb.

[0004] The invention comprises the use of a combination of two or more metals or a single metal in multiple metallic states to combine properties

of both low and high oxidation state metals. This allows for removal of a broad range of contaminants. Oxidizable contaminants are absorbed on the high oxidation state portion of the material and reducible contaminants are absorbed on the low oxidation state portion of the material. The selection and ratios of metals is dependent upon the source of CO_2 to be decontaminated in conjunction with the contaminants to be removed.

[0005] The method comprises both decontamination of the CO_2 and regeneration of the canisters or beds to both reduce cost and facilitate the method of the invention. Purification comprises contacting the fluid CO_2 with the adsorbent for sufficient time to allow for decontamination. Parameters such as time, flow rate, temperature are determined based on the source gas and the apparatus available. Regeneration serves to return the adsorbents substantially to their original state. Regeneration involves both oxidation, to remove sulfur and other contaminants, and reduction, to prepare materials for oxygen adsorption. Metals are selected that are oxidized and reduced under various conditions to allow for the reduction of one of the adsorbents while retaining the other adsorbent in an oxidized state. Exact methods for regeneration depend on the type of beds, the adsorbents used and the major contaminants in the CO_2.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] Figure 1 is an O2 removal test manifold;

[0007] Figure 2 is purifier temperature data; and

[0008] Figure 3 is oxygen removal efficiency data.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

[0009] The invention is a method for the production of highly purified CO_2 containing contaminants at $\leq$ 5 ppb, preferably $\leq$ 1 ppb, most preferably $\leq$ 0.1 ppb, for use in the semiconductor industry. Contaminants of primary concern are O_2, sulfurous contaminants, especially COS, silicon containing contaminants and light hydrocarbons (LHC, $\leq$ 4C). Contaminants of secondary concern are nitrogenous compounds, especially NH_3 and NO_x and

other organic compounds.

[0010] The invention comprises the use of a mixture of two or more metals or metallic states as adsorbents. The adsorbents combine properties of both high and low oxidation state metals. This combination can be accomplished by a number of methods. First, two or more metals in different oxidation states can be combined (e.g. Cu/ZnO, Fe/MnO_x). Second, two or more metals in similar oxidation states with sufficiently different properties can be combined (e.g. NiO/TiOx, PdO/CeO_x). Third, a single metal which has oxidation states that vary throughout the metal can be used (e.g. VO_x). Considerations for selecting the appropriate adsorbent or adsorbents are discussed in the Examples below.

[0011] Regardless of the specific selection of adsorbents, the materials are an intimately co-mingled mixture prepared by impregnation, co-precipitation, sublimation or other relevant techniques. The materials may be supported on or mixed with an inorganic oxide for increased surface area, greater structural integrity, improved flow rate, or to accommodate other physical and mechanical considerations. In a preferred embodiment, the adsorbent has a surface area of at least 50 m^2/g, should be able to withstand the high pressure associated with all three fluid phases of CO_2 and should not become entrained in the fluid stream or introduce additional contaminants into the fluid stream. The use of co-mingled adsorbents allows for the removal of a variety of contaminants in a single step rather than having to perform multiple steps of decontamination through different beds or containers.

[0012] A variety of purification apparatuses are known including, but not limited to canister and multiple and single bed apparatuses. In a preferred embodiment, the method of the invention is carried out using a dual bed apparatus. Purification comprises contacting the adsorbent material with the CO_2 stream for sufficient time to allow decontamination to the desired level. Decontamination considerations such as time, pressure, flow rate and temperature may be readily determined by those skilled in the art. Decontamination is alternated with regeneration. Frequency and duration of regeneration varies depending on the size of the adsorbent surface area, the

level of contamination of the gas source and a number of other factors well known to those skilled in the art. Regeneration involves oxidation to prepare the material for adsorption of sulfurous and other contaminants and reduction to prepare the material for oxygen adsorption. The exact process of regeneration is dependent upon the adsorbents used and the contaminants that were removed from the CO_2. Such considerations are discussed in the Examples below.

EXAMPLE 1

[0013] *Adsorbents containing two or more metals present in different oxidation states.* Combinations of metals such as Cu/ZnO and Fe/MnO_x are examples. Advantageous materials are those in which the higher oxidation-state portion of the material is reactive towards certain contaminants (e.g. by removing COS in a metathesis reaction that generates CO_2), while the lower oxidation-state portion of the material is reactive towards certain other contaminants (e.g. by absorbing oxygen, hydrogen, or carbon monoxide). Particularly advantageous materials are those in which oxygen readily binds to an oxygen deficient portion of the material (e.g. for kinetic reasons), then diffuses into a co-mingled portion of the material which preferentially binds oxygen (e.g. for thermodynamic reasons). The ratios of the adsorbents to each other can be widely varied depending on the contaminants to be removed as well as other parameters known to those skilled in the art.

[0014] Cu/ZnO is known to exist as a combination of metallic copper and zinc oxide with Cu present in a substantially reduced state. ZnO is stable fully oxidized Zn^{II} and metal oxides adsorb LHCs. Reactions can proceed as follows during the CO_2 purification method:

$$Cu^0 + \tfrac{1}{2} O_2 \rightarrow CuO$$

$$ZnO + COS \rightarrow ZnS + CO_2$$

$$MO_x + LHC \rightarrow (MO_x \bullet LHC)$$

Thus, LHCs are removed from the CO_2 stream.

[0015] Similar reactions are possible using Fe/MnO_x, a material which has the properties of a substantially metallic iron mixed with iron and

manganese oxides in widely varying oxidation states. Oxygen-deficient Fe reacts with O_2 and Fe and manganese oxides remove sulfur containing contaminants from the CO_2 stream.

$$2FeO + \frac{1}{2} O_2 \rightarrow Fe_2O_3$$

$$MO_x + COS \rightarrow MO_{x-1} + CO_2$$

[0016] The combination of Fe/MnO is ideal for the removal of all non-methane hydrocarbons (NMHC) and is particularly suited for the migration of chemisorbed oxygen and sulfur from Fe into bulk Mn.

EXAMPLE 2

[0017] *Adsorbents containing two or more metals present in similar oxidation states, but in which the two metals vary considerably in chemical properties.* Combinations of metals such as NiO/TiOx and PdO/CeO_x are examples. The aforementioned adsorption properties are still relevant to this material, wherein two portions of the material have different, complementary adsorption properties (e.g. different electronegativities). Rather than the different adsorption tasks being accomplished by similar metals with an oxidation state differential, different portions of the material are in relatively the same oxidation states. The different adsorption properties come from the presence of vastly different metals. An example is a mixture of a late transition metal oxide with an early transition metal oxide. As in the previous case, especially advantageous materials are those that undergo a degree of self-regeneration by diffusion of contaminants adsorbed in one portion of the material into another portion of the material. The ratios of the adsorbents to each other can be widely varied depending on the contaminants to be removed as well as other parameters known to those skilled in the art.

[0018] TiOx may have oxygen vacancies or be able to adsorb oxygen on exposed metallic active sites. Reactions can proceed as follows during the CO_2 purification method:

$$TiO_x + \frac{1}{2} O_2 \rightarrow TiO_{x-1}$$

$$Ti^{*}O_x + O_2 \rightarrow [TiOx{\bullet}O_2]$$

This form may involve bridging dioxygen acting as a ligand rather than

undergoing a redox reaction on a partially reduced titania surface.

[0019] NiO also may be substantially or partially reduced to Ni^0, in which case redox chemistry may take place involving the Ni-containing portions of the material. Additionally, the NiO may participate in sulfur scavenging as shown in the following reactions:

$$NiO + COS \rightarrow NiS + CO_2$$

[0020] Nickel sulfides/oxides are also known to undergo further disproportionation reactions such as the reaction shown below:

$$xNiO + NiS \rightarrow Ni(SO_x) + x\ Ni^0$$

which may generate additional reduced nickel active sites. The ability of NiO to adsorb LHC had not been demonstrated prior to the instant invention. (See Example 5)

$$NiO + LHC \rightarrow (NiO{\bullet}LHC)$$

[0021] The various oxidation states of the oxygen-deficient oxides of CeO_x are well-known. Their reactivity is relatively unexplored, but is likely similar to TiO_x and TiO_2 as shown above. Pd and PdO are well known on ceria and display reactivity towards various contaminants in a manner similar to Ni which is in the same periodic group. The combinations of materials in this example function similarly to those of the previous example by providing different reactivities resulting in different adsorption and regeneration properties.

EXAMPLE 3

[0022] *Adsorbents containing a single metal oxide in which the metal oxidation state varies throughout the metal.* VO_x is an example of such a metal. The aforementioned adsorption properties are still relevant to this material, wherein two portions of the material have different, complimentary adsorption properties (i.e. different oxidation states). The same metal present in different oxidation states within the material accomplishes the different adsorption tasks. For example, a low oxidation state portion of the material may adsorb oxygen, while a higher oxidation state portion may preferentially

adsorb LHCs or sulfurous contaminants.

[0023] Vanadia based materials in which vanadium is present in several incremental oxidation states are known. For example:

$$VO + 1/2\ O_2 \rightarrow VO_2 \rightarrow V_2O_3 \rightarrow V_2O_5$$

Vanadium sulfides, analogous to the vanadium oxides are also possible. The electropositive surface of vanadia is similar to titania, but with different oxidation characteristics, allowing the reaction:

$$VO_x + LHC \rightarrow (VO_x{\bullet}LHC)$$

for the adsorption of LHCs.

[0024] The level of oxidation of vanadium can be controlled during the regeneration process of the invention.

EXAMPLE 4

[0025] *Regeneration of adsorbents.* Regeneration of the adsorbents decreases cost and facilitates the use of the method of the invention. As combinations of metals and metallic states are selected to have various decontamination properties, they are also selected to have different regeneration properties to allow for all of the contaminants to be purged from the adsorbent using heat or cooling in combination with oxygen, followed by reduction under specific conditions to allow only a portion of the adsorbent to undergo reduction.

[0026] An example of this type of reaction would be to first contact the material with an oxidant regeneration gas (e.g. O_2) for a sufficient time and a sufficient temperature to effect removal of all oxidizable contaminants, followed by a second contact with a reductant regeneration gas (e.g. H_2) for sufficient time and at sufficient temperature to produce the desired composition of the material.

[0027] A second example of regeneration encompasses both of the above regeneration steps into a single step. A mixture containing an amount of H_2, an amount of H_2O and the balance inert gas is contacted with the adsorbent for a sufficient time at a sufficient temperature to return the adsorbent to essentially its original state. This one step regeneration process

saves both time and money.

EXAMPLE 5

[0028] *Oxygen removal efficiency of nickel media exposed to gaseous carbon dioxide.* An analysis was performed to demonstrate that Ni media can remove O_2 from gaseous CO_2. The test purifier consisted of a 70KF body filled with Ni media. The purifier was activated under the same conditions as the inert purifier. Afterwards, the purifier was purged with pre-purified CO_2. The temperature was monitored to indicate when the Ni was done reacting with the CO_2.

[0029] Figure 1 represents the experimental setup. Porter mass flow controllers (MFCs) controlled the flow rates of the 944ppm O_2 standard (Air Products) and the pre-purified house N_2 to attain the desired concentrations. A backpressure regulator (AP Tech) was used to vent during purging of the test manifold. A Nanotrace Oxygen Analyzer (Delta-F) was used to measure the O_2 concentration. The second pre-purified house nitrogen line was used to purge the instrument. A rotameter (Porter) controlled the pressure during the experiment.

[0030] The purifier was tested under the following conditions:

- Challenge Concentration = 1 parts per million (ppm) of O_2
- Flow rate = 3 standard liters per minute (slm)
- Pressure = 30 psig
- Temperature = Ambient

Initially, the challenge gas is allowed to flow through the bypass to the instrument. After 10 minutes the purifier is placed online.

[0031] Figure 2 shows the data gathered when the reduced Ni was exposed to CO_2. The supposition was that the Ni media was fully conditioned with CO_2 when the purifier returned to room temperature.

[0032] Figure 3 shows the data gathered from the Nanotrace. The purifier removed O_2 below 10 parts per billion (ppb) in less than 90 minutes. From extrapolating the data, an O_2 concentration of 5ppb was reached within

3 hours. The purifier has maintained an O_2 concentration below 5ppb for 66.3hours.

[0033] Although an exemplary embodiment of the invention has been described above by way of example only, it will be understood by those skilled in the field that modifications may be made to the disclosed embodiment without departing from the scope of the invention.

ABSTRACT

The invention is a method for the decontamination of CO_2 to a sufficient level of purity to allow it to be used in the semiconductor industry. The invention comprises the exposure of fluid CO_2 to a combination of metals or metallic states under the appropriate conditions for removal of contaminants. The adsorbents are then decontaminated and reduced to allow further rounds of decontamination. The adsorbents are selected to be complimentary to each other, preferentially adsorbing different contaminants. Additionally, the adsorbents are selected to undergo reduction differently such that upon regeneration only a portion of the metals are reduced and the adsorbent is returned essentially to its original state.

Figure 1

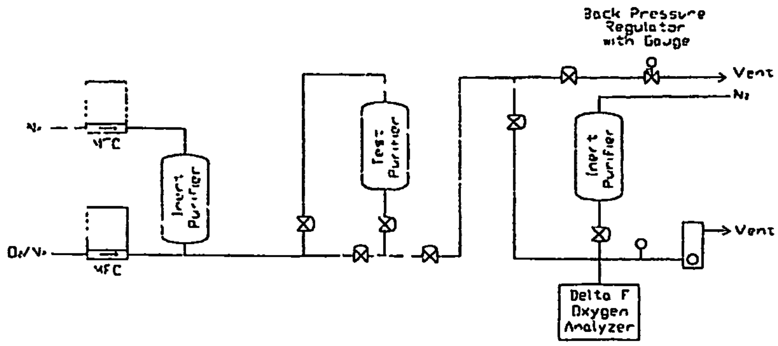

Figure 2

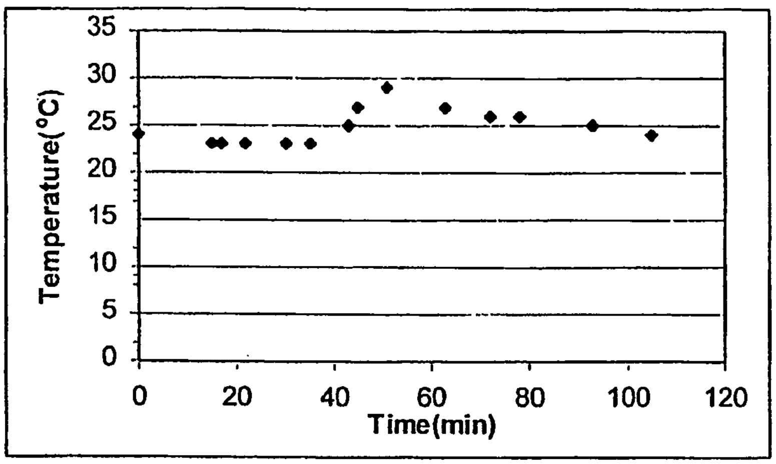

Figure 3